

available evidence suggests that isomerization of dehydro-peptides occurs to some extent in the solid state. A mechanism for the radiation-induced isomerization of the $\sim\text{CO}-\text{NH}\sim$ linkage in solid peptide systems has recently been described⁵. A detailed report of the various aspects of the radiation chemistry of the cyclic dipeptides will be forthcoming.

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CHEMISTRY

Binding of Xenon to Halogens, to Alkali Metals, and to Itself

THE existence of stable XeF_4 and XeF_2 molecules has recently been demonstrated¹. A description of the binding and molecular geometry using the conventional electron pair model has been proposed². Twelve of the XeF_4 electrons are assumed to be distributed in four electron pair bonds and two sets of lone pairs. This model is based on analogies with the chemistry and geometry of a large number of inorganic compounds. Simple chemical analogy must likewise predict that molecules such as $\text{Xe}(\text{Cs})_4$ or $\text{Xe}(\text{Rb})_4$ will not exist. Be_2 offers a partial analogy to Xe_2 and implies that the latter molecule will not be bound.

It is also important to understand XeF_4 in terms of approximate solutions to Schrödinger's equation, and an explanation based primarily on our knowledge of the electronic structure of isolated atoms and ions has been given³. The xenon fluoride bond is attributed to the atomic distortion⁴ produced by electron correlation and the resultant opportunity for a xenon electron of one spin to partially fill the outer shell of a fluorine atom to a slightly greater extent than its partner of opposite spin.

However, in many quantum mechanical problems we find an inherent symmetry between systems possessing closed shells plus one electron and those possessing closed shells minus one electron, and thus we must examine the binding of $\text{Xe}(\text{Cs})_4$ and $\text{Xe}(\text{Rb})_4$ relative to that in XeF_4 . In addition to numerous atomic calculations there exists one *ab initio* molecular calculation which can aid our discussion. This is a wave function for HeH determined by Harris⁵, and we may use it as a model for the binding of xenon to an alkali metal atom. His wave function is particularly important because it was carried out by the full permutation group method, thus allowing different orbitals for different spins and building in the correlation induced orbital distortions that have been used to explain binding in XeF_4 (ref. 3).

Harris's HeH calculation shows no binding and we can interpret this through the properties of the constituent atoms. First, the noble gas atoms will have absolutely no electron affinity—even though there is a slight correlation induced separation of α and β spin there can be no stable orbit for an additional electron—so that the ease with which an alkali metal atom loses an electron has no influence on potential binding. Second, the electron affinity of both hydrogen and the alkali metal atoms is considerably less than fluorine. On the other hand, it

might be argued that the unfilled s shell of hydrogen could provide as favourable a potential energy environment for a rare gas electron as does fluorine. This reasoning is incorrect, however, since not only is the electron affinity less but also the hole in the fluorine has a p -like angular dependence and the partially unpaired xenon electron which is most available for bonding also has a p -like angular distribution. Similarly, Xe_2 cannot exist because xenon shows no tendency to accept an electron.

One of the principal purposes in presenting this article is to point out the paucity of detailed theoretical knowledge available on the electronic structure of even small molecules, and short of very elaborate and extensive *ab initio* calculations (which are just now on the outer edge of feasibility for XeF_4 and XeF_2) it is not possible at present to give a thoroughly convincing theoretical prediction of inert gas compounds. In hindsight it appears that the geometry of XeF_4 is the same as ICl_4^- and thus empirical or semi-empirical model calculations bring out and tend to support the similarity in electronic structure of these compounds at their equilibrium separation⁶. However, there does not now exist any really adequate connexion between the effective Hamiltonians of the simple model schemes (such as the simple LCAO MO method) and direct solutions of Schrödinger's equation. Particularly at larger atomic separations, the xenon-fluoride bond involves subtle correlation effects and the partial breakdown of the simple idea of closed shells which are not directly represented in calculations with the simple models. Certainly a major reason for the lack of extensive investigations into inert gas compounds has been the overwhelming success of the Periodic Table based on free atoms along with the concept of closed shell configurations in organizing chemical experience.

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Breeding of Nuclei

IN 1911 Miers¹ wrote: "I have many times noticed that when the appropriate crystal is introduced into a super-saturated solution, which is not strong enough to crystallize spontaneously, it may cause crystals to grow not only in actual contact with itself, but at some little distance in its neighbourhood". McCabe² has also discussed this subject: other references are rare. It is proposed to refer to this phenomenon as 'breeding' of nuclei. We have recently studied this question experimentally, using aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and have concluded that various categories of breeding may be observed.

(1) If a crystal from a stock bottle is dipped into an under-cooled solution, a considerable number of small crystals appear after only a few seconds, usually on the bottom or surface of the solution. The breeding in this case is believed to be due to detached crystallites present on the surface of the crystal, which were produced either by rapid evaporation of solution when the crystal was dried, or by mechanical impact. This form of breeding will be called 'initial' breeding.

(2) If however the crystal, after removal from the bottle, is pretreated by growing at a low under-cooling (say 1°C)